Statistical Thermodynamics in Chemistry and Biology

Statistical thermodynamics

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January 12, 2017

What is statistical thermodynamics?

The microscopic world

- The microscopic world is described by quantum mechanics; the Schrödinger equation:

$$\hat{H}\psi_i = \varepsilon_i \psi_i$$

  where ε_i is the energy of state i.
- For matter, terms like atoms, molecules, and electronic states are key concepts.

The macroscopic world

- The macroscopic world is described by thermodynamics.
- A system is described in terms of pressure, density, temperature, free energy, etc.

Statistical thermodynamics

Statistical thermodynamics provides the connection between the microscopic and macroscopic worlds. It gives the possibility to determine thermodynamics properties from molecular (quantum mechanical) models.

An example of a statistical mechanical model

- The temperature, T, is a macroscopic property and an experimental observable that may be written as an average:

$$T = \langle T \rangle = \langle T(t) \rangle = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} T(\tau)$$

  where we emphasize that it is an average in $\langle T \rangle$ and an average over time, t in $\langle T(t) \rangle$. τ_{obs} is the number of observations.

- In particular,

$$T = \frac{2\langle K \rangle}{3Nk_B}$$

  where k_B is Boltzmann's constant and the kinetic energy, K, is given by classical mechanics as a sum over all the particles, N, as

$$K = \sum_{i=1}^{N} \frac{m_i v_i^2}{2}$$

  and can be calculated at each observation.